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Formation of silica nanotubes through a TPPS J aggregates template

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It is found that 5,10,15,20-tetrakis (4-sulfonatophenyl) porphyrin (TPPS), which is known to form J aggregates in water under low pH value, acts as a template for the hydrolyzing of organosilane. The nanotube structures of silica with 4–8 nm inner diameters are obtained, which is consistent with the height of TPPS J aggregates, indicating that TPPS J aggregates are indeed acting as the template for the sol-gel transcription. The TPPS J aggregation disappear when the medium pH value is shifted from acidic to basic, consequently formed silica nanostructures are amorphous nanosphere rather than nanofiber structures. In contrast, the copper phthalocyanine (TSCuPc), which does not exist as linear J aggregates, cannot induce the silica to form one dimensional nanofiber structures, implying that the templating effect of TPPS J aggregates for inorganic nanostructures.

J aggregates, sol-gel transcription, silica nanostructures

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Porphyrin aggregation has gained much attention for over half a century, owing to its interesting optical and electronic properties exhibited by its self-assembled nanostructures [1–3]. In this field, a water-soluble tetrakis(4-sulfonatophenyl) porphyrin, TPPS, is well studied, because its diacid species can form J aggregates under aqueous conditions [4–8], high ionic strength, and can be induced by other cationic species including polypeptides [9–12], ionic liquid [13,14], surfactant and polyelectrolyte [15]. At acid aqueous, the TPPS exists as a zwitterionic state with peripheral SO_3^{2-} groups and cationic pyrrole ring resulting from the protonation of the pyrrole nitrogen. Then the π–π stacking between overlapping phenyl rings and electrostatic interactions between the negative sulfonate groups and the protonated pyrrole nitrogen atoms are the main driving force for the J aggregation of TPPS. The formation of TPPS J aggregates is usually characterized by a sharp and intense absorbance at 490 nm (J-band) which shows a large red shift relative to the monomer absorption at about 434 nm (the soret band). Corresponding Q-band at about 600–700 nm also shows red shifted and enhancement in intensity relative to the monomer as the result of aggregation of H_2TSPP [2–16]. A great deal of techniques, including RLS [17], small-angle X-ray scattering (SAXS) [18], atomic force microscopy (AFM) [19], and scanning tunneling microscopy (STM) [20] has proved aggregates form nanorod structures where the individual TPPS molecules are arranged in a head-to tail fashion.

Thus, the linear aggregates are the suitable candidate for the synthesis of some fibriform polymer or inorganic structures. For example, Shinkai reported that the assembly of TPPS acts as a template for electropolymerization of aniline, EDOT and pyrrole on the ITO electrode [21–23]. The corresponding monomers grow up to a nanosized rod-like structure (30–50 nm in diameter and several hundred nanometers in length), reflecting the aggregation mode of TPPS. In addition, TPPS supermolecules can act as a template to transcribe its organic superstructures into inorganic materials by a sol-gel reaction of metal alkoxides (sol-gel transcription), by which one can control the morphology of inorganic compounds and create various new superstructural inorganic materials. Che transcribed the organic structure into chiral mesostructured porphyrin-silica hybrid using a

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cationic organolsilane by a sol-gel reaction [24]. She used a cationic organosilane bearing a quaternary ammonium group to interact with anionic TPPS and then cohydrolyze with tetraethyl orthosilicate. Here, TPPS assembly was functioned as a template to prepare silica nanostructures. Since TPPS assemblies are very sensitive to the pH, the silica nanostructure obtained by the sol-gel method may depend on the TPPS aggregates by the variation of pH. In addition, in order to verify the template effect of TPPS J aggregates, we used CuPc as a reference, which cannot form J aggregates at the same condition. There was no fiber structure can be obtained when CuPc was used as a template, indicating that the silica fiber structures was transcribed from liner J aggregates.

1 Materials and method

1.1 Materials

Tetrakis(4-sulfonatophenyl)porphyrin (TPPS), was purchased from Dojindo Laboratories and used without further purification. 3,4,4,4-Tetrasulfonic acid tetrasodium salt copper phthalocyanine (TS-CuPc) was used as received. The scheme of zwitterionic TPPS and CuPc are shown in Scheme 1. Hydrochloride and NaOH were used to adjust the pH value of TPPS or CuPC solution. 3-Aminopropyltriethoxysilane (APES) and tetraethyl orthosilicate (TEOS) were purchased from Alfa Co. The molecular structures of TPPS, TS-CuPC, TEOS and APES are shown in Scheme 1.

1.2 Preparation of SiO_2 nanostructures through TPPS assembly as a template

In the experiments for preparing SiO_2 nanostructures, TPPS solutions were prepared using Millipore water (18 MΩ cm) and the pH was adjusted by hydrochloric acid and NaOH. The APES and TEOS in which the ratio is kept at 1∶10 were added into TPPS solution and further vigorous stirring for 3 h. The mixture was incubated at room temperature for 5 d. And then the mixtures were collected by centrifugal separation and washed with water at least five times in order to remove TPPS.

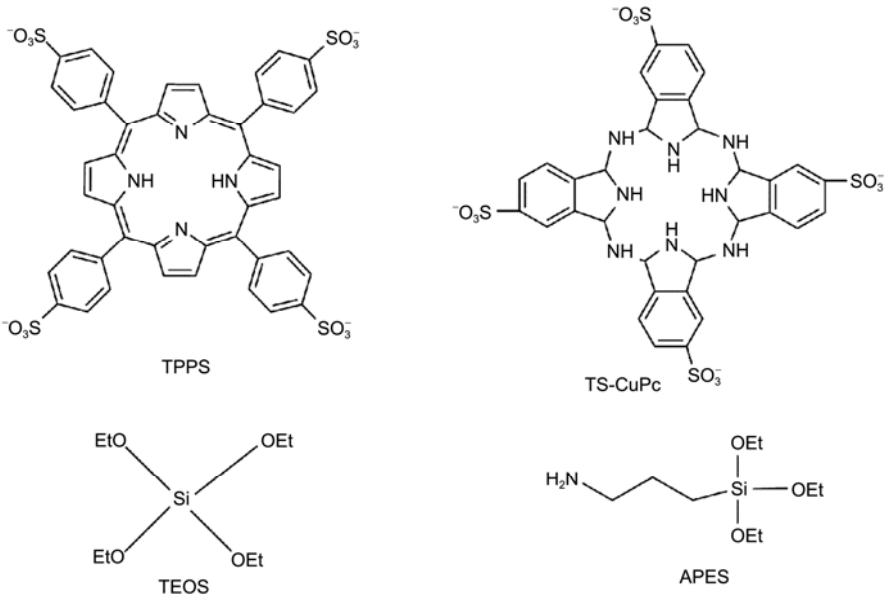
1.3 Characterization

The absorption spectra were obtained from a JASCO UV-550 spectrophotometer. SEM (scanning electron microscope) was performed using a Hitachi S-4800 system with an accelerating voltage of 15 kV. Samples for SEM were prepared by cast the nanostructure aqueous dispersion on silicon slices. TEM (transmission electron microscope) images were obtained on a JEM-100CX II electron microscope operating at an accelerating voltage of 100 kV. EDX was used to measure the elemental analysis of TiO_2/SiO_2 composite. The TEM samples were prepared by placing a small amount of silica nanostructure dispersion on carbon-coated copper grids (300 mesh).

2 Results and discussion

2.1 SiO_2 nanostructures obtained by TPPS template

The protonation of the pyrrole nitrogen takes place upon decreasing pH below about 5, while the sulfonic acid groups remain unprotonated until much lower pH [25]. Then at pH 3 (1×10^{-5} mol/L), the TPPS exist as a zwitterionic species, characterized by the Soret and Q bands at 434 and 644 nm, respectively, as shown in Figure 1. These bands show



Scheme 1 Structures of TPPS, TS-CuPc, TEOS and APES.

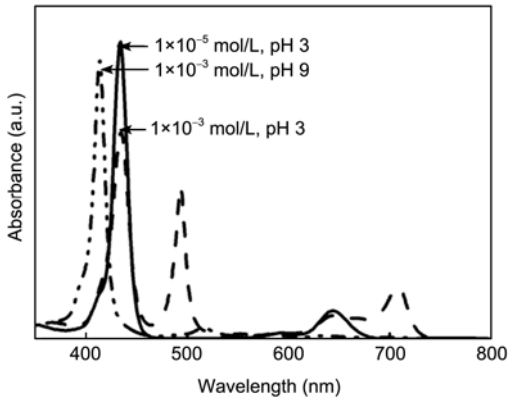


Figure 1 UV-Vis absorption spectra of TPPS solution at different pH: The 490 and 704 nm absorbances are assigned to the J aggregates transition. The 1.0 cm and 1.0 mm path length cell were used for the measurement of TPPS (1×10^{-5} mol/L) and (1×10^{-3} mol/L), respectively.

red-shift relative to the adsorption band of free TPPS (414 nm). Upon increase the concentration to 1×10^{-3} mol/L, the new bands appeared at 491 and 702 nm, respectively, indicating the formation of TPPS J aggregates. When the pH value is above 7, the soret band shifts to 414 nm, accompanying the disappearance of adsorption band at 490 and 702 nm, indicating the TPPS exists as a free base monomer with a net −4 charge. In the free base TPPS, peripheral phenyl rings are perpendicular to the plane of the porphyrin ring, while the protonation of the pyrrole nitrogen at lower pH value causes phenyl groups are closer to being in plane with the porphyrin ring. The change in conformation of phenyl group causes the blue-shift of adsorption band from zwitterionic species to free base, and also disturb the disassembly of TPPS aggregates.

The APES with equal molar amount to TPPS and ten times TEOS was added into TPPS solution. After subsequent stirring for 3 h, the mixture was kept at room temperature for 5 d. Figure 2(a) shows a SEM image of the formed silica nanostructures in the presence of 1×10^{-5} mol/L TPPS (pH 3). Some amorphous nanosphere structures can be observed. In the case of 1×10^{-3} mol/L TPPS at pH 7 (Figure 2(b)), the similar nanosphere structures with the radius of 400–500 nm can be obtained. When the system pH value decrease to 3 (Figure 2(c)), some intertwined nanofiber structures with 20–30 nm in width and several to tens of micrometers in length appears.

Since the APES used here is a kind of weak base, which can influence TPPS assembly, we explored that the TPPS aggregates in the presence of variation of APES concentration and the corresponding silica nanostructures. Figure 3 shows that the UV spectra of TPPS (1×10^{-3} mol/L, pH 3) upon variation of APES concentration. As we mentioned above, the TPPS exists as J aggregates at this condition. Upon addition of APES into the TPPS solution (pH 3, 1×10^{-3} mol/L), when the ratio of APES to TPPS below 2, the J aggregates still exist, characterized by the TPPS

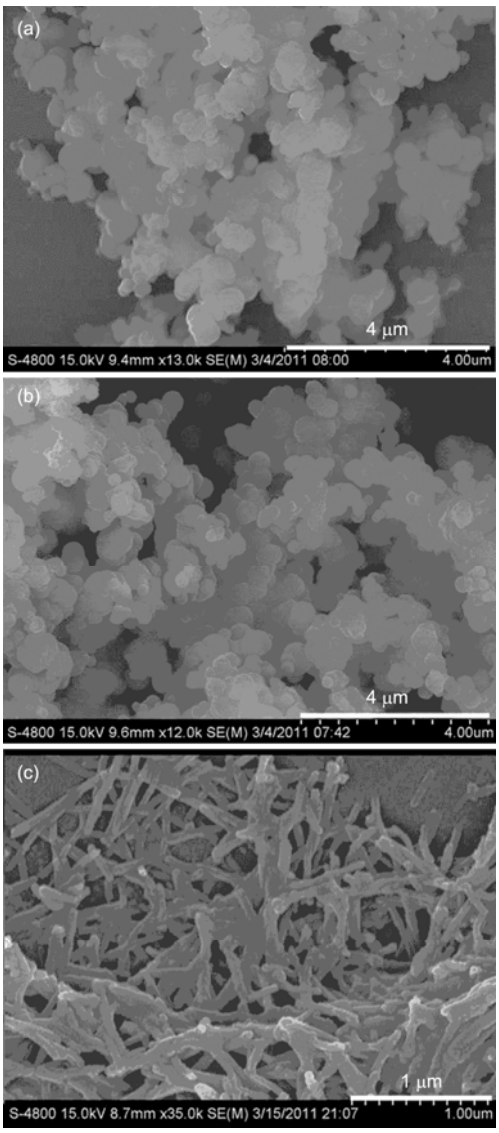


Figure 2 The formed silica nanostrucures in the presence of TPPS (a) 1×10^{-5} mol/L, pH 3; (b) 1×10^{-3} mol/L, pH 7 and (c) 1×10^{-3} mol/L, pH 3.

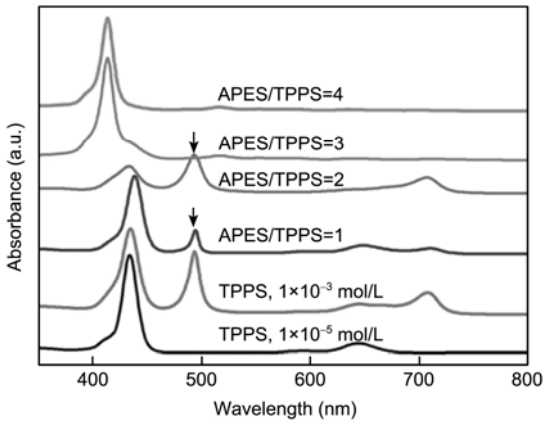


Figure 3 UV-Vis spectra of TPPS at variation of APES. A 1.0 cm and 1.0 mm path length cell were used for the measurement of TPPS (1×10^{-5} mol/L) and (1×10^{-3} mol/L), respectively.

J-band at 490 nm. While the ratio of APES increase to 3 and 4, the J aggregates of TPPS were changed to free base species as the result of the unprotonation of pyrole NH by NH_2 group of APES. The color of TPPS changed from green to dark purple with the increase concentration of APES, indicating the unprotonation of TPPS.

Figure 4 shows that the morphology of silica nanostructures induced by TPPS assembly at variation APES ratio. The nanofiber structures of TPPS J aggregates are transcribed into the silica nanostructure (Figure 4(a) and (b)). The nanosphere structures are obtained when the ratio of APES increased to 3, in which the TPPS exists as free base monomers. TEM revealed that the silica nanofiber structures are actually composed nanotubes, and the inner diameters are within 4–8 nm, as shown in Figure 5(a) and (b). TPPS J aggregates morphology was ever imaged by AFM

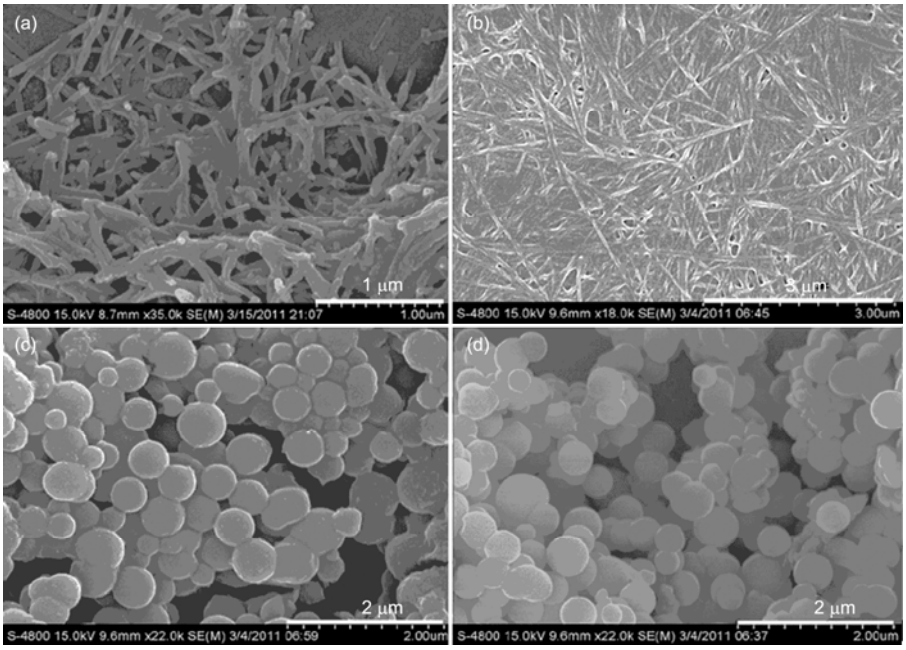


Figure 4 SEM images of formed silica nanostructures in the presence of TPPS (1×10^{-3} mol/L, pH 3) at variation of APES to TPPS ratio (a) 1; (b) 2; (c) 3 and (d) 4.

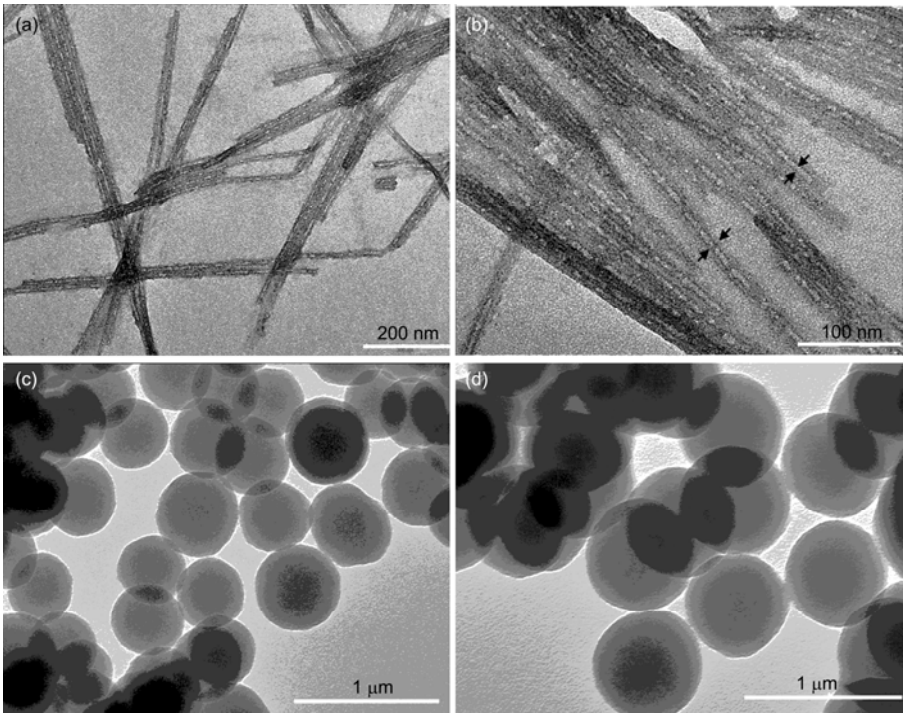


Figure 5 TEM images of formed silica nanostrucures in the presence of TPPS (1×10^{-3} mol/L, pH 3) at variation of APES to TPPS ratio (a) 1; (b) 2; (c) 3 and (d) 4.

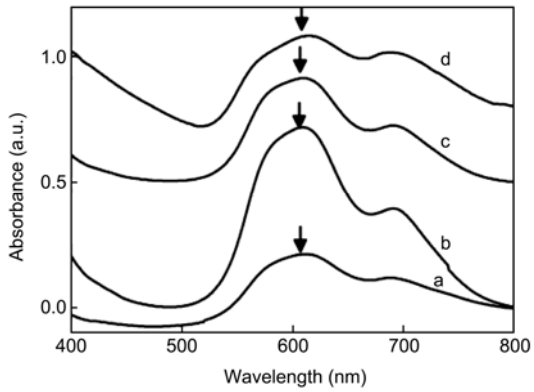


Figure 6 UV-Vis spectra of TS-CuPc (a) dilute solution (1×10^{-6} mol/L); (b) concentrated solution (1×10^{-3} mol/L); (c) 1×10^{-3} mol/L TS-CuPc solution (pH 3) with APES (the ratio of APES to TS-CuPc is 1) and (d) 1×10^{-3} mol/L TS-CuPc solution (pH 3) with APES (the ratio of APES to TS-CuPc is 4).

using mica, HOPG or Au(111) as substrates, and the nanorod structures with 18–40 nm for the width and 4–10 nm for the height were reported in the literature [20]. The height of nanorod is consistent with the inner diameter of silica nanotube, indicating that the TPPS J aggregates were indeed acted as the template for the hydrophisis. In the case of the ratio of APES to TPPS increasing to 3 and 4, the NH_2 moiety of APES resulted in the unprotonization and the finally the disassembly of J aggregates, consequently the silica nanotube structures disappeared. Some solid nanosphere structures with the diameter around 400–500 nm was obtained. This result further reveals that the linear J aggregates of TPPS can be transcribed into inorganic structure by sol-gel method.

2.2 SiO_2 nanostructures obtained in the presence of CuPc

In order to further prove the templating effect of TPPS J aggregates for inorganic nanotube structures, the CuPc was used as a reference. Figure 6 shows that UV-Vis spectrum of CuPc and the complex of CuPc with APES/TEOS. Spectrum a in Figure 6 shows the visible absorption spectra of a dilute aqueous solution of TS-CuPc (1×10^{-6} mol/L). The large peak in the region 550–700 nm corresponds to a Q-band. The Q-band in the dilute aqueous solution is split in two, 671 and 610 nm, which can be ascribed to the monomer absorption (671 nm) and aggregate adsorption (610 nm). The latter can be attributed to absorption by dimmers or higher aggregates. The peak at 671 nm corresponds to the amorphous state in which adjacent molecules adopt no particular orientation with respect to one another. Spectrum b in Figure 6 corresponds to the concentrated solution of TS-CuPc(C=1×10^{-3} mol/L, pH 3). The adsorption band shows a dominant maximum at 610 nm and a shoulder peak at 690 nm. This suggests that the peak at lower wavelengths corresponds to molecular aggregates, cofacially stacked dimmers and oligomers [26,27]. When APES and TEOS were added into the TS-CuPc solution, the shape of spectrum was similar with the absence of APES and TEOS, with the relative intensity adsorption of cofacially stacked aggregates

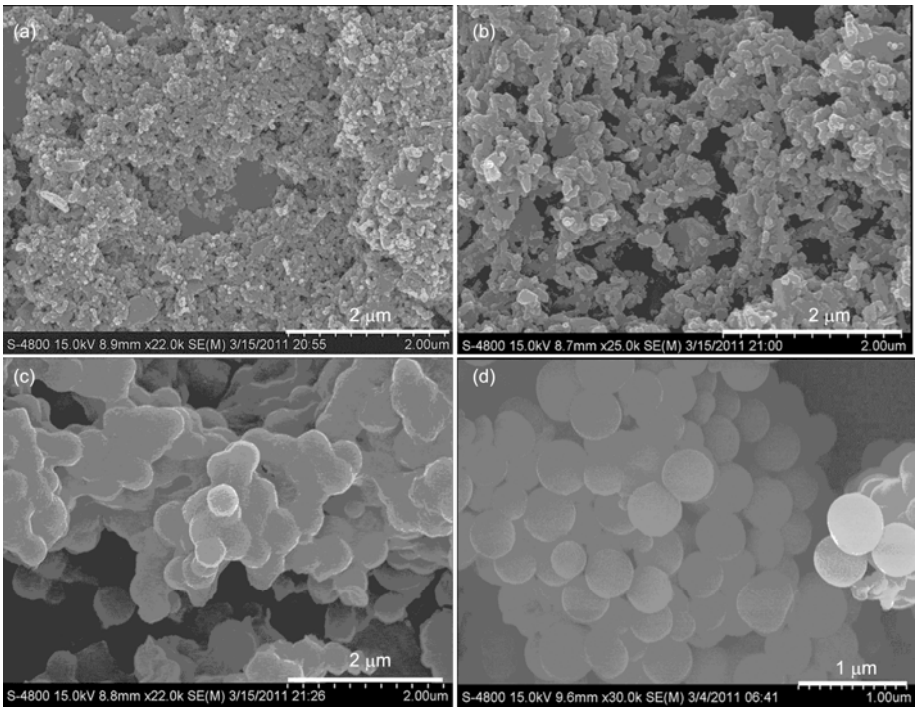


Figure 7 SEM images of formed silica nanostrucures in the presence of TS-CuPc (1×10^{-3} mol/L, pH 3) at variation of APES to TS-CuPc ratio (a) 1; (b) 2; (c) 3 and (d) 4.

slightly lower. These results indicate that TS-CuPc cannot form J aggregates at aqueous solution and in the presence of APES. When the hydrolysis of APES and TEOS was executed at CuPC solution, the nanosphere structures can be obtained at the ratio of APES to TPPS from 1 to 4. In other words, there is no one dimensional nanofiber structures can be obtained, support that the linear structure of J aggregates playing an important role in the synthesis silica nanofiber structures.

3 Conclusions

TPPS J aggregates are important supramolecular system, and here we have demonstrated that they can act as the template to prepare silica nanostructures. The SEM and TEM images showed that the nanotube structures only can be obtained in the presence of J aggregates. And the inner diameter of the nanotube is consistence with the height of nanorod of TPPS J aggregates revealed by AFM image, further indicating that the TPPS aggregates structures can be transcribed into inorganic structures. In contrast, the TS-CuPC, which does not form linear J aggregates, cannot induce the silica to form one dimensional nanofiber structures. Therefore, this is a novel transcription process of supramolecular templates to inorganic materials.

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